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STUDY PROGRAM TO IMPROVE FUEL CELL PERFORMANCE BY PULSING TECHNIQUES

2ND QUARTERLY REPORT

2 January, 1964

Technical Management
Auxiliary Power Generation Office
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio
Mr. W. J. Nagle

Contract NAS3-2752

Period Covered: October 1 - December 31, 1963

UNION CARBIDE CORPORATION
DEVELOPMENT DEPARTMENT
PARMA RESEARCH LABORATORY
PARMA, OHIO

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Prepared by

M. L. Kronenberg
Project Leader

2324523

UNION CARBIDE CORPORATION
~~DEVELOPMENT DEPARTMENT~~
PARMA RESEARCH LABORATORY
P. O. Box 6116 - Cleveland 1, ~~Ohio~~

Parma, Ohio

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1.0 PURPOSE

This investigation is concerned with what effect the modification of the gas-electrolyte interface will have on the performance of fuel cell electrodes. The interface will be disturbed by electrical and mechanical pulses over a wide range of frequencies.

Hydrophobic and hydrophillic electrodes will be used in this investigation.

2.0 ABSTRACT

15862 Author

Experiments involving mechanical pulsing of the electrolyte in the range 0 to 425 c.p.m. were completed on carbon and on thin, composite electrodes. The gaseous fuels used in these experiments were hydrogen, oxygen and air. Polarization data were taken before, during, and after pulsing. The results indicated that in this frequency range and at pressure amplitudes ranging from 9 to 24 psia, the main effect was an accelerated "breaking-in" phenomena for the electrodes themselves rather than a significant modification in the three-phase reaction zone during pulsing.

Experiments involving the mechanical motion of electrodes have been started on carbon electrodes. Preliminary results at 60 cycles/second indicate that under these conditions the main effect, here too, is an accelerated breaking-in phenomena for the electrodes.

Electrical pulsing experiments comparing interrupted d.c. with continuous d.c. at the same average current were completed for carbon and for thin, composite electrodes. The results for 60-cycle/second interruption, 6 seconds/cycle interruption and a slow current reversal cycle (5 minute discharge; 10 second charge) were all virtually the same. There was no significant difference in life or performance between the electrodes tested and the control electrodes.

A new Teflon cell was designed and is presently under construction for pulsing the electrolyte at sonic frequencies. Author

3.0 MEETINGS AND CONFERENCES

G. E. Evans, K. V. Kordesch, and M. L. Kronenberg of Union Carbide met with E. M. Cohn, R. L. Cummings, H. J. Schwartz and W. J. Nagle of NASA at Union Carbide Parma Research Laboratory on December 16, 1963 to discuss the progress and scope of the contract. The meeting was continued on the following day with Prof. T. J. Gray of Alfred University and several other members of the NASA staff also present. The purpose of this second meeting was to provide an opportunity for a free exchange of ideas between Prof. Gray (who is investigating electrical pulsing at porous electrodes) and members of Union Carbide and NASA who are interested in pulsing experiments on porous electrodes.

It was agreed that Union Carbide Corporation would continue the program outlined in our First Quarterly Report. To facilitate comparisons between results obtained from electrical pulsing experiments at Alfred University, and the electrical, mechanical and sonic pulsing experiments conducted at Union Carbide, it was agreed to commonly use hydrophillic (metal) electrodes. Prof. Gray is already employing these electrodes.

4.0 FACTUAL DATA

4.1 Mechanical Motion of Electrolyte.

4.1.1 Test Equipment.

The Teflon cell used for pulsing experiments, which was described in the First Quarterly Report, was replaced by an improved polystyrene cell which is virtually transparent. This makes it possible to observe the electrodes while they are being assembled and thus insure proper gasketing and electrode contact.

4.1.2 Experimental Results.

Electrodes run in the Teflon cell showed voltage fluctuations of more than 20 mv during the electrolytic pulsing, as was reported previously. When the tests were conducted in the polystyrene cell, it was observed that the electrolyte level changed considerably during pulsing. The electrolyte level was then increased by putting an extension tube on the cell. With the electrolyte level established safely above the electrodes practically all the fluctuations disappeared.

The normal procedure was to run a polarization curve before pulsing, followed by a scan of pulsing speeds at constant current and a polarization curve after pulsing. In Figures 1 and 2 in the Appendix are shown the scanning curves for 1/4-inch and thin anodes and cathodes at a constant current of 40 ma/cm^2 for pulsing frequencies of 0 to 341 c. p. m. The voltage readings are resistance-free values taken with a 60-cycle interrupter. This experiment was repeated on four sets of electrodes and the results were reproducible. The two readings given at 0 c. p. m. represent measurements before and after pulsing. 12 Normal KOH electrolyte was used in all experiments.

In Figures 3 through 5 are shown representative resistance-included polarization curves taken before, during and after pulsing on 1/4-inch carbon electrodes at two pressure amplitude settings.

In general, the results on 1/4-inch and thin electrodes indicated that normally the most significant change in electrode performance took place between the prepulsing run and the first pulsing run. While the change was only on the order of several millivolts it normally resulted in higher anodic polarization and lower cathodic polarization. No special effects were noted during pulsing or at a particular pulsing frequency, but the performance seemed to be related mainly to pulsing time. This indicated that the effect of pulsing on the electrode itself appears to be mainly an accelerated "breaking-in" phenomena. All mechanical pulsing data will be tabulated after results on the third type of electrode (hydrophillic metal electrodes) have been completed.

4.2 Mechanical Motion of Electrodes.

4.2.1 Test Equipment.

This test was conducted by coupling the plunger of a continuous-duty solonoid directly to the electrode plate. The plunger vibrated because it was restrained from closing completely. In the experiments conducted thus far, the solonoid was driven at 60 cycles/second at various amplitudes by means of a Variac. For other frequencies an audio-signal generator and amplifier will be used.

4.2.2 Experimental Results.

In Figures 6 and 7 are presented preliminary polarization curves taken before, during, and after vibrating at an amplitude setting of 60. Here, again, the results appeared to be only a "breaking-in" effect on the electrodes themselves. The polarization changes observed were several millivolts or less for the vibration experiments completed thus far.

4.3 Electrical Pulsing.

The results obtained from electrical pulsing experiments are summarized in Table I. The experimental conditions are tabulated in the left-hand columns and the changes in potential between the initial and final test day for the control cells and test cells are given in the far right-hand columns. For 1/4-inch carbon electrodes the average voltage changes agreed within 3 millivolt. For thin, composite electrodes the voltage changes for the pulsed electrodes averaged 24 mv lower than for the control cells. This observed difference, however, is still within the standard deviation of the test results, indicating that pulsing has had no significant effect.

TABLE I

RESULTS OBTAINED FROM ELECTRICAL PULSING EXPERIMENTS

Type of Electrode	Cycle	No. Days on Test	Average Current Density (ma/cm^2)	Initial Potential Control Cell	Initial Potential Test Cell	Final Potential Control Cell	Final Potential Test Cell	mv Change from Initial Potential Control	mv Change from Initial Potential Test
1/4-Inch Carbon	60 cycle/sec. Interrupted	20	10	.898	.902	.939	.936	+41	+34
"	"	20	50	.846	.843	.863	.858	+17	+15
"	"	15	10	.947	.953	.939	.921	-8	-32
"	"	15	50	.899	.897	.862	.863	-37	-34
"	"	26	10	.953	.913	.960	.912	+7	-1
"	"	26	50	.915	.879	.884	.861	-31	-18
"	6 sec. on - 6 sec. off.	15	50	.890	.887	.814	.839	-76	-48
"	"	15	50	.887	.887	.854	.839	-33	-48
"	5 min. charge 10 sec. discharge	28	25 discharge 2.5 charge	.854	.839	.743	.749	-111	-90
Thin Electrodes, Normal Wetproofing	60 cycle/sec. Interrupted	22	10	.939	.933	.949	.946	+10	+13
"	"	22	50	.892	.900	.909	.885	+17	-15
Thin Electrodes, Heavy Wetproofing	"	22	10	.904	.897	.910	.877	+6	-10
"	"	22	50	.799	.806	.788	.771	-9	-35
Thin Electrodes, Normal Wetproofing	5 min. discharge 10 sec. charge	20	25 discharge 2.5 charge	.851	.833	.880	.790	+29	-43
"	"	20	"	.851	.849	.880	.811	+29	-38
"	"	15	"	.819	.780	.833	.846	+14	+66
"	"	15	"	.785	.799	.859	.834	+74	+35

5.0 FUTURE WORK

The electrical pulsing and mechanical pulsing experiments that have been conducted thus far on carbon and on thin, composite electrodes will be carried out on standard metal electrodes.

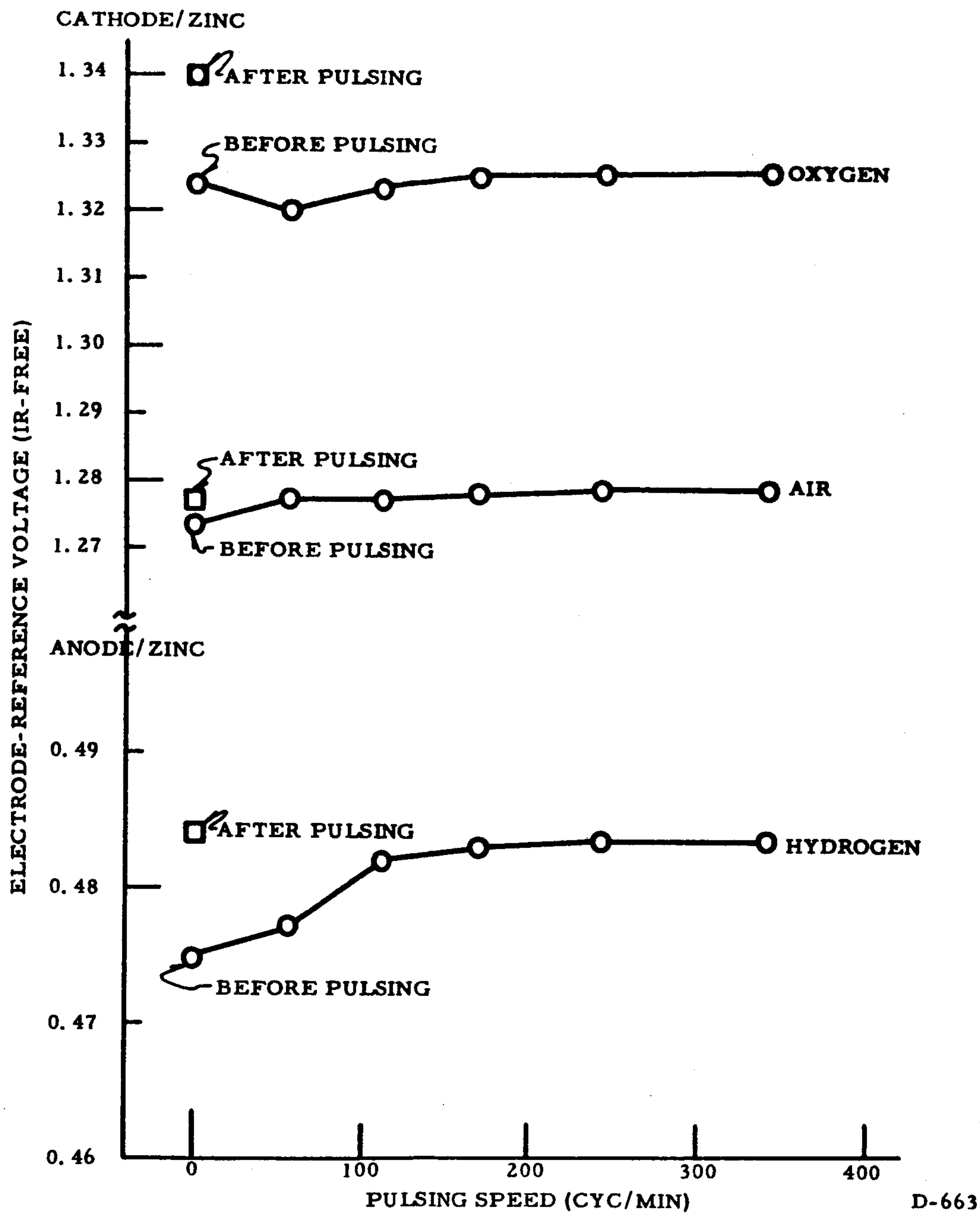
Sonic electrolyte pulsing and electrical pulsing experiments involving alternating current superimposed on direct current will also be carried out during this coming period.

MLK/jdh

M. L. Kronenberg

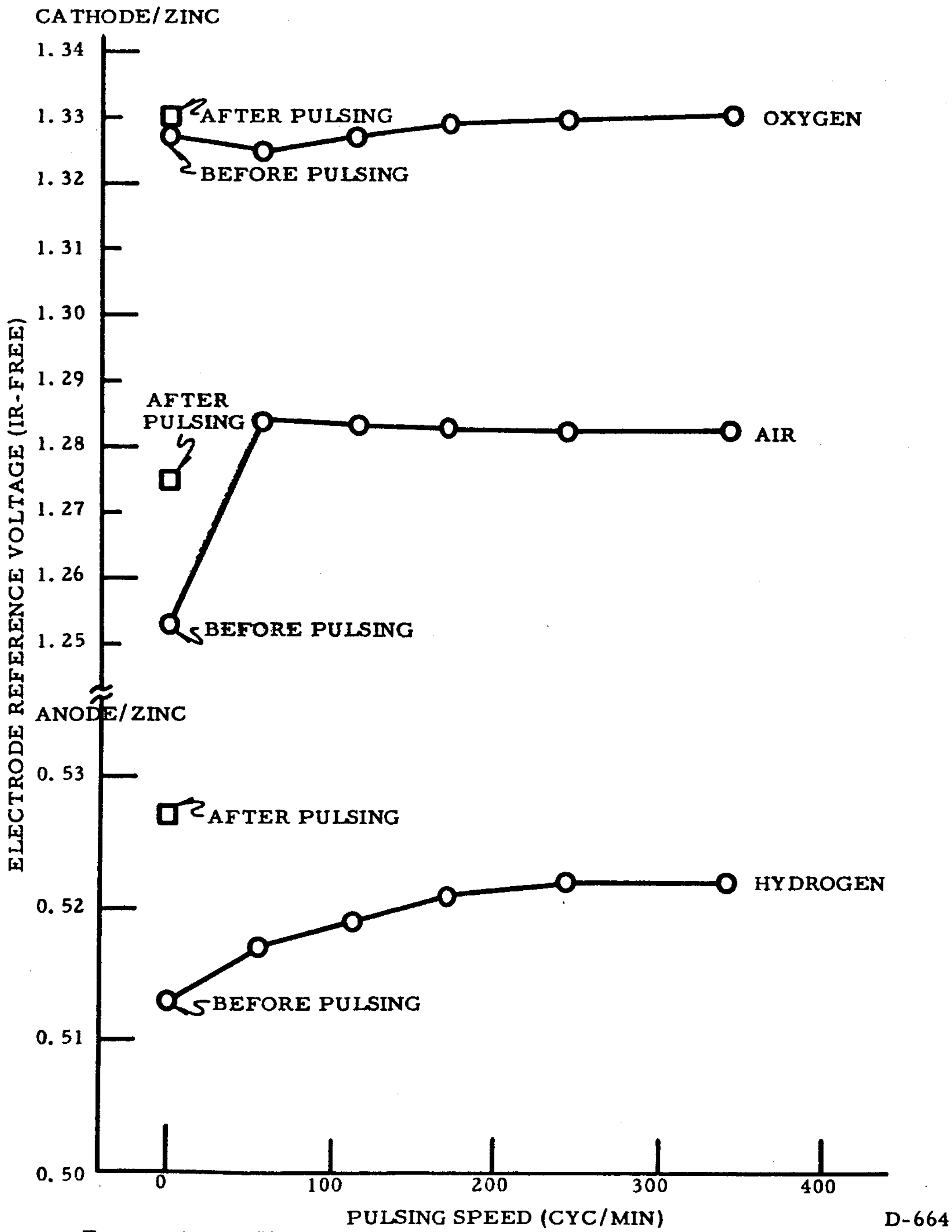
M. L. Kronenberg
Project Leader

APPENDIX



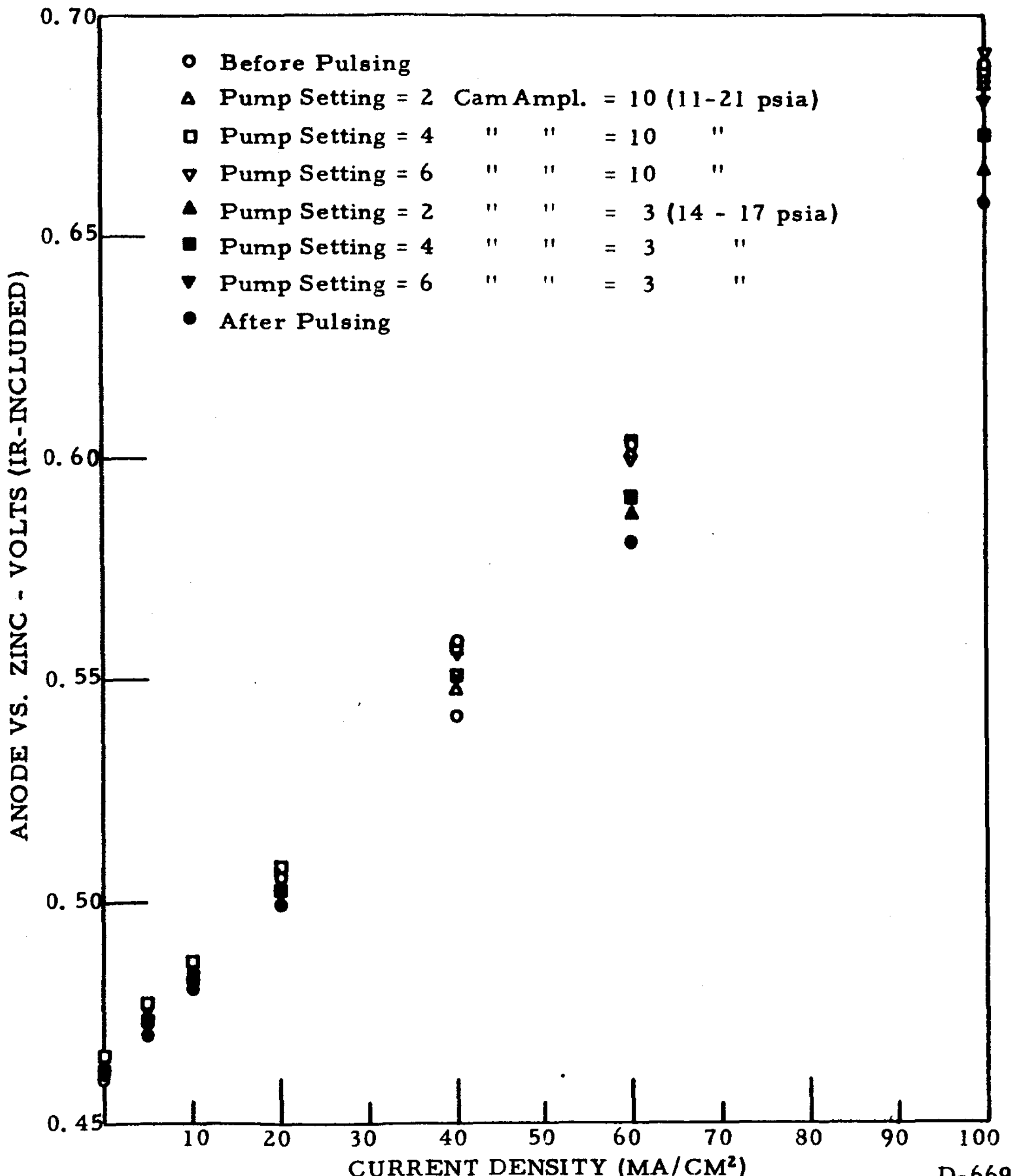
Temperature: 45°C
Current Density: 40 ma/cm²
Electrodes: 1/4" Carbon
Pressure amplitude setting = 10 (approx. 11 to 21 psia)

Fig. 1 Electrode-Reference Potential as a Function of Pulsing Speed.



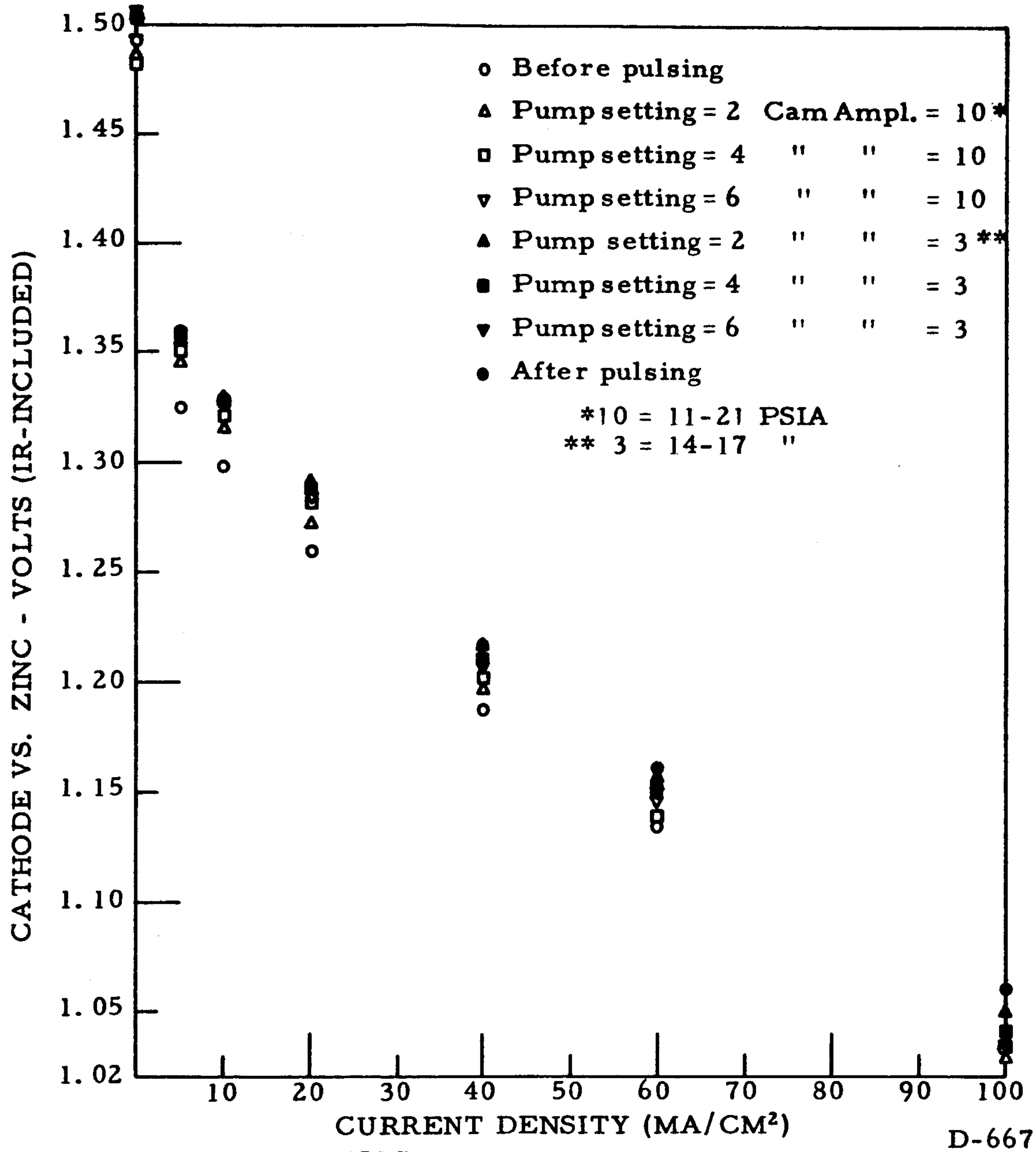
Temperature: 45°C
Current Density: 40 ma/cm²
Electrodes: Thin, composite.
Pressure amplitude setting = 10 (approx. 11 to 21 psia)

Fig. 2 Electrode-Reference Potential as a Function of Pulsing Speed.



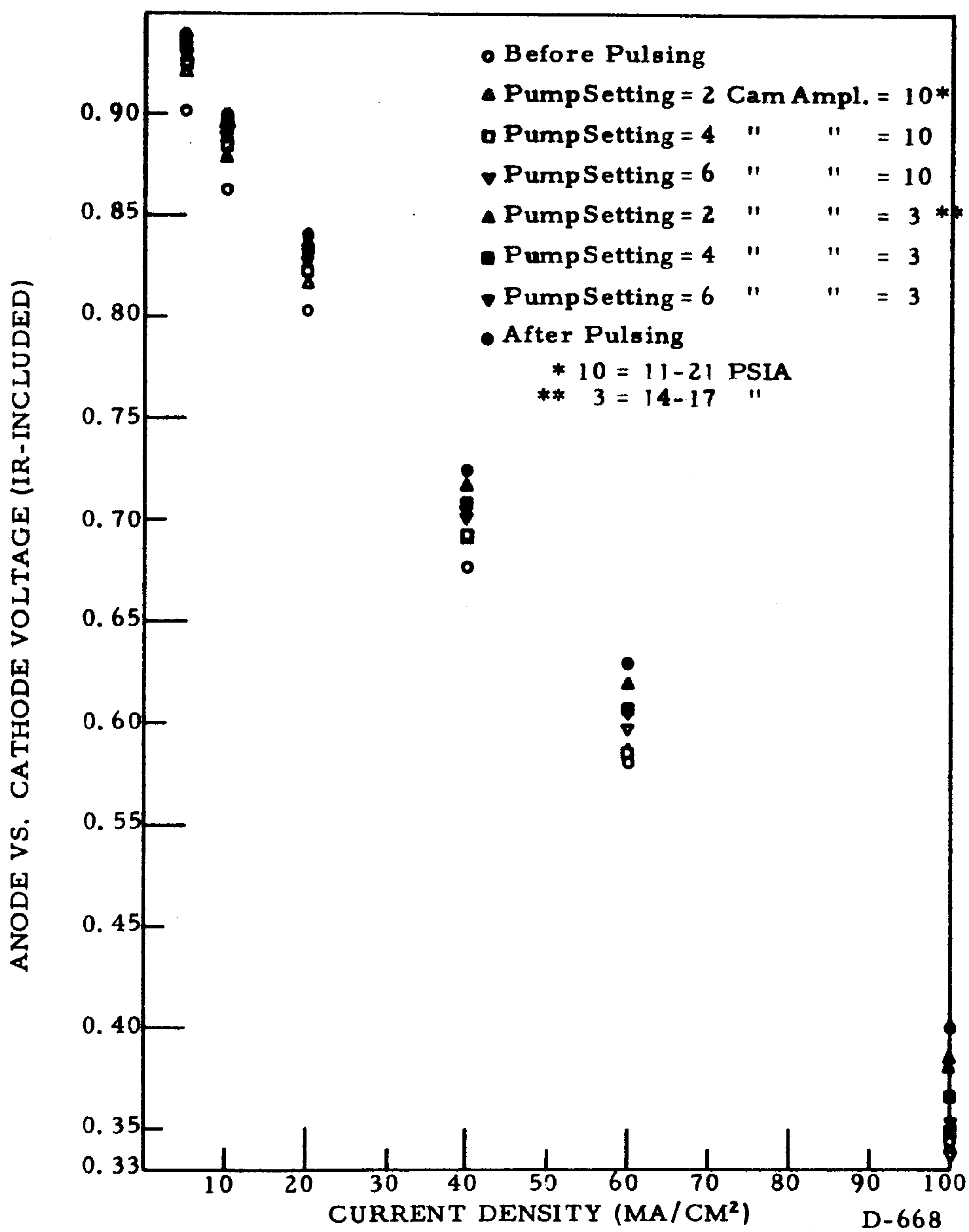
Temperature: 45°C
Electrodes: 1/4" Carbon
Anode Fuel Gas: Hydrogen

Fig. 3 Anode-Reference Polarization Curves; Before, During and After Pulsing.



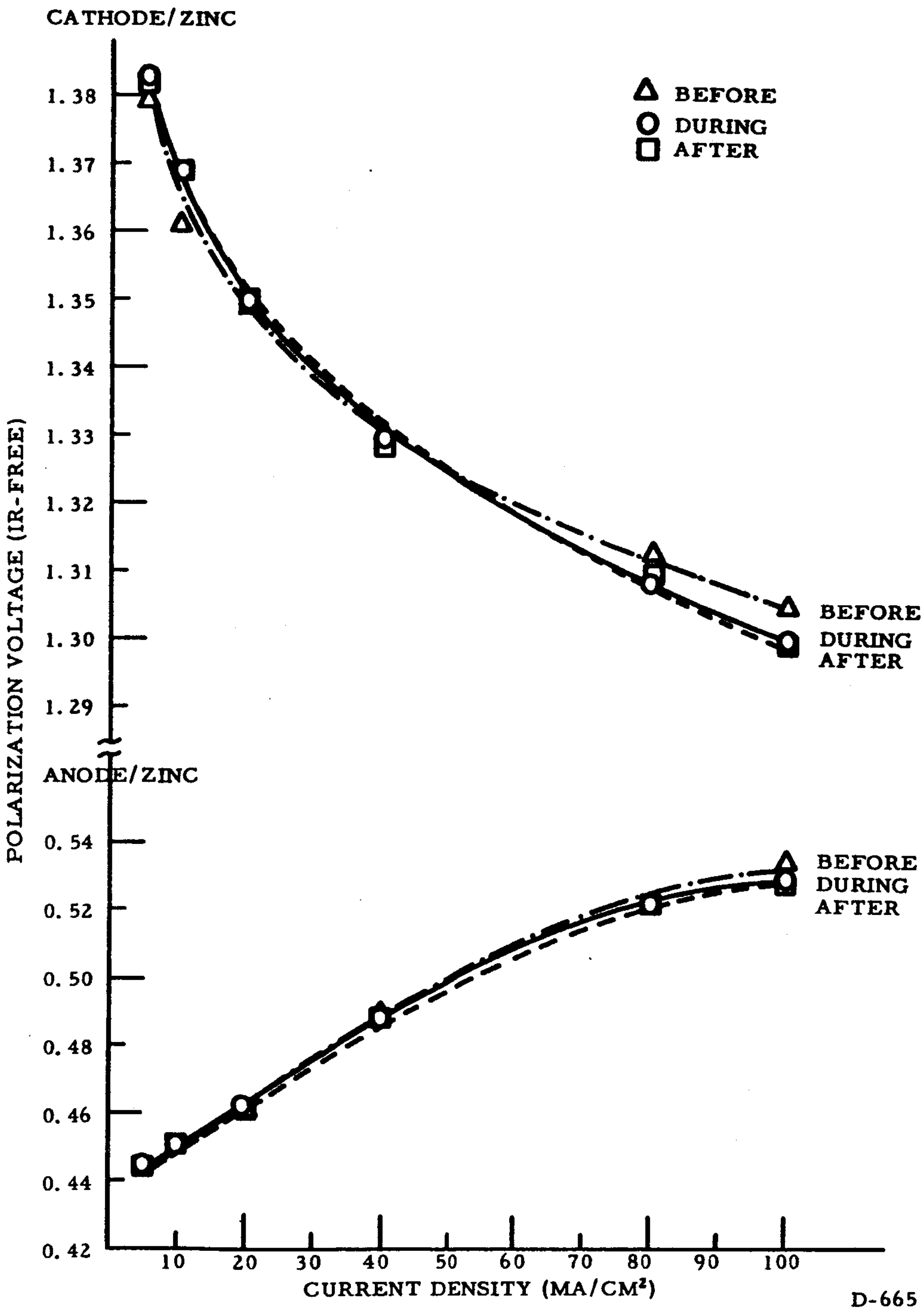
Temperature: 45°C
Electrodes: 1/4" Carbon
Cathode Fuel Gas: Oxygen

Fig. 4 **Cathode**-Reference Polarization Curves; Before, During and After Pulsing.



Temperature: 45°C
Electrodes: 1/4" Carbon
Anode Fuel Gas: Hydrogen
Cathode Fuel Gas: Oxygen

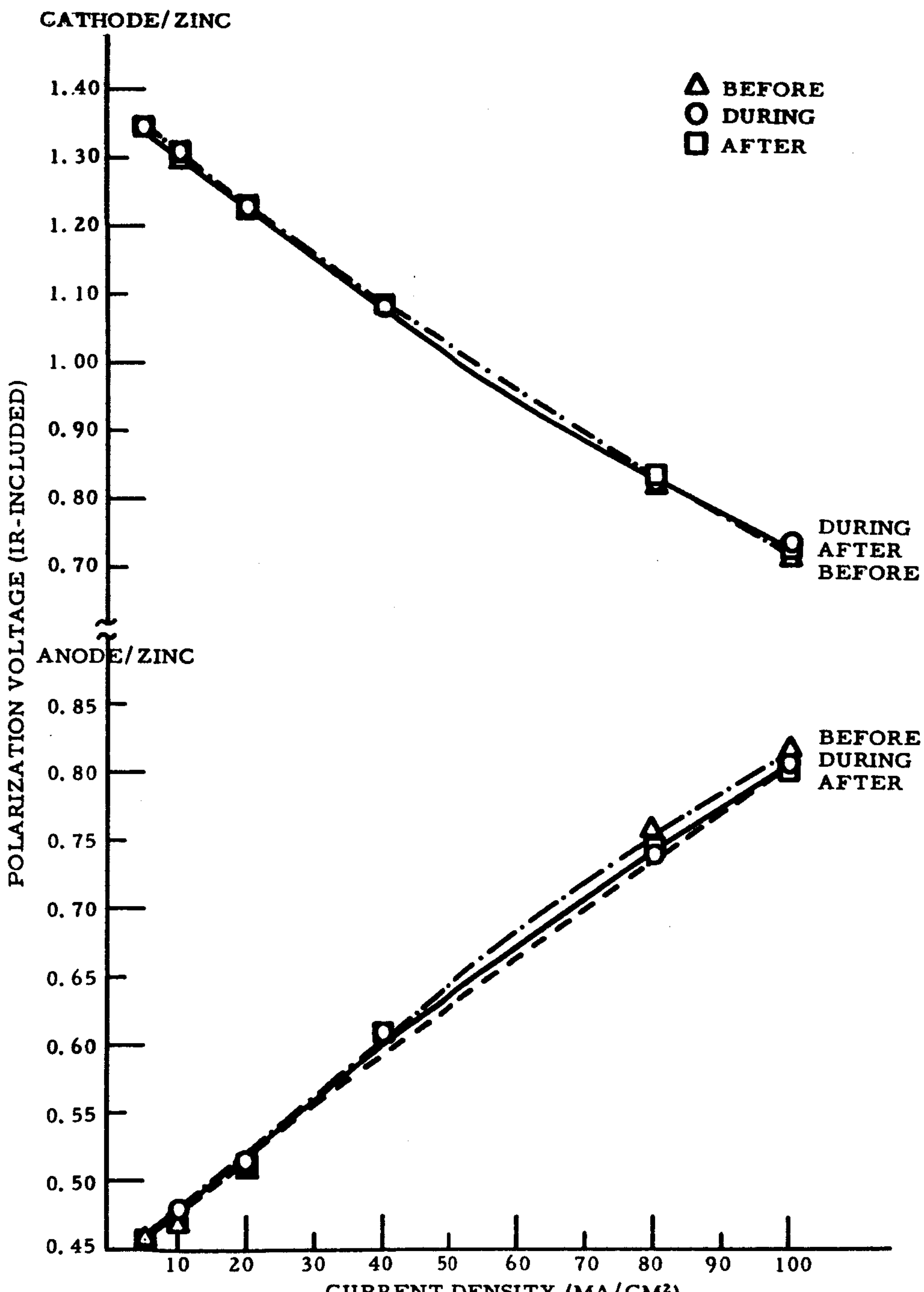
Fig. 5 Anode-Cathode Polarization Curves; Before, During and After Pulsing.



Temperature: 50°C
Electrodes: 1/4" Carbon
Anode Fuel Gas: Hydrogen
Cathode Fuel Gas: Oxygen

Vibration Frequency: 60 c. p. s.
Amplitude Setting: 60 (Variac setting)

Fig. 6 Polarization Curves Before, During and After Vibration Tests. (IR-Free)



Temperature: 50°C
Electrodes: 1/4" Carbon
Anode Fuel Gas: Hydrogen
Cathode Fuel Gas: Oxygen

Vibration Frequency: 60 c.p.s.
Amplitude Setting: 60 (Variac setting)

Fig. 7 Polarization Curves Before, During and After Vibration Tests. (IR-Included)

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